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NICOTINE INSECTICIDES. Part VII--SEARCH FOR SYNERGISTS

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The search for compounds to replace some of the nicotine in insecticides and thus make its use more economical has been continued. This paper reports results with 100 chemicals that were tested similarly to those discussed in Parts II and V of this series (E-709 and E-768). The materials were furnished by the Eastern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry and were tested at the Anaheim, Calif., laboratory of the Bureau of Entomology and Plant Quarantine.

Material and Methods

A dust containing 2 percent of nicotine sulfate and 5 percent of adjunct was compared with a 5-percent nicotine sulfate standard for leaf-feeding larvae or a 3.5-percent standard for the pea aphid. The mortality caused by some mixtures was compared with that induced by the two components when used separately. The comparisons were made at approximately the same deposit. All mixtures were diluted with attapulgite.

Some of the materials were chosen at random, but most of them were selected because of close chemical resemblance to phthalonitrile and bis(p-chlorophenyl) sulfide, the two best materials discussed in E-768.

The test insects included third instars of the armyworm (Pseudaletia unipuncta (Haw.)) and the diamondback moth (Plutella maculipennis (Curt.)), fourth instars of the green dock beetle (Gastrophysa cyanea Melsh.), and the second nymphal stage of the pea aphid (Macrosiphum pisi (Kltb.)).

All the larvae were fed dusted foliage in 9-cm. petri dishes, whereas the aphids were dusted directly on the plants on which they were feeding and then confined in battery jars 16.5 cm. in diameter and covered with

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1/ Formerly the Division of Control Investigations.

cloth caps. In preliminary fumigation tests the insects were placed in the lower half of a petri dish, a filter paper 11 cm. in diameter dusted with the toxicant was placed over the dish, and the top half put in place. This makes a rather close fitting fumigation chamber and, in addition, keeps the insects from coming into contact with the insecticide. For all tests the deposits ranged from 75 to 200 micrograms per square centimeter. Approximately 35 larvae and 40 or more aphids were used in each test. Each material was tested against 3 or 4 species. Mortality counts of the larvae were made after 3 days and those of the aphids after 1 day.

Phytotoxicity tests with the materials showing the most promise were made on plants of bean, beet, broccoli, celery, collard, eggplant, lettuce, pepper, swiss chard, and tomato.

Discussion of Results

A material was considered to be a possible synergist for nicotine if the mortality caused by a mixture of the two (table 1, column A) was approximately the same or above that caused by the nicotine standard (B). If synergism was indicated in tests against two or more species of insects, the material was later subjected to developmental testing. The materials in table 1 were selected on this basis and their evaluations can be found in the A - B column. This table also presents mortalities caused by dusts containing 2 percent of nicotine as the sulfate (C) and in some cases 5 percent of adjunct (D) when used alone. Column A - (C + D) shows the difference between the kill produced by the mixture and the additive kills of nicotine and adjunct when tested separately.

On the basis of the averages of mortalities of all tests the materials in table 1 compared favorably with the 5-percent standard, except tall oil nitrile (Arneel TOD), bis(p-bromophenyl) sulfide, and bis(p-chlorophenyl) disulfide. Of the materials on which a preliminary determination could be made for the presence of synergism (A - (C + D)), alpha-naphthonitrile and methyleneaminoacetonitrile were good. A single test with bis(p-chlorophenyl) disulfide against the pea aphid did not show promise.

Alpha-naphthonitrile is a volatile material and in a fumigation test a 5-percent dust of it killed 64 percent of the armyworms. Fluorene when mixed with nicotine sulfate was as effective as the standards against the armyworm and the pea aphid, but no further tests were made, since its continued use is dangerous to the investigator.

Phytotoxicity tests showed that against five varieties of plants methyleneaminoacetonitrile, tall oil nitrile, and bis(p-chlorophenyl) disulfide were not injurious at 1-percent concentrations. Phenyl sulfoxide, m-nitrobenzonitrile, and monochlorodibenzothiophene caused considerable burning, while 2-chlorodibenzothiophene and Aroclor 1232 caused moderate injury. Tests were not made on the other adjuncts given in table 1.

Adjuncts in mixtures with nicotine that showed synergism against one insect only are shown in table 2.

From the data presented six adjuncts were chosen for quantitative testing--isophthalonitrile, methyleneaminoacetonitrile, alpha-naphthonitrile, tall oil nitrile, bis(p-bromophenyl) sulfide, and bis(p-chlorophenyl) disulfide.

The following adjuncts in mixtures with nicotine showed no synergism against the armyworm, the diamondback moth, and the pea aphid:

Acenaphthene
Adiponitrile
m-Aminobenzonitrile
gamma-Aminoisobutyric acid
Anthracene
Benzonitrile
Benzothiazole, 2-mercapto-
Benzoylacetonitrile
di-n-Butylcyanamide
n-Capronitrile
Calcium gluconate
Carbazole
Chloracetonitrile
p-Chlorobenzonitrile
beta-Chloropropionitrile
Cyanoacetamide
Dibenzothiophene, 2,8-dichloro-
Diethyl fumarate
1,1-Dimethyl-2-acetylethylene oxide
Dimethyl fumarate
5,5-Dimethylhydantoin
Dimethyl maleate
Ditolyl sulfide
2-Ethyl-1-hexanol
Ethyl beta-phenyl-alpha-cyanoacrylate
Furfuryl alcohol
Glycolonitrile
3-Hydroxy-3-methyl-2-butanone
Iso-capronitrile
Isophorone
beta-Isopropoxypropionitrile
Itaconic acid
Metaldehyde
1-Methylnaphthalene
2-Methylnaphthalene
1-Methyl-2-propene-1-ol
1-Methyl-2-propene-1-ol-acetate
Myrcene
beta-Naphthoylacetonitrile
Paraldehyde
Phenol, 2,2-methylenebis [4-chloro-
Phenol, 2,2-methylenebis [4,6-dichloro-
gamma-Phenoxybutyronitrile
Phenylacetonitrile
beta-Phenypropionitrile
Phenyl sulfide, 4-hydroxy-
Phenyl sulfide, 4-hydroxy-4'-methyl
Phenyl sulfide, 4-methoxy-4'-methyl
Phenyl sulfone, 5,5'-dichloro-2-2'-dihydroxy
Phenyl sulfone, 4 methoxy-
Propionitrile
Red oil nitrile (Arneel ROD)
Stearonitrile (Arneel 18D)
Succinonitrile
Tetrahydrofurfuryl acetate
Tetrahydrofurfuryl alcohol
Thianthrene, 2,6-dichloro-
m-Tolunitrile
o-Tolunitrile
p-Tolunitrile
alpha, alpha, beta-Trichloro-propionitrile
s-Trioxane
n-Valeronitrile
Veratraldehyde
p-Xenyl sulfide

Table 1.--Mortality caused by dusts containing adjuncts that show promise as synergists for nicotine

Adjunct and insect	Deposit of dust mixture (micrograms per square centimeter)	Extent of feeding	Percent mortality					
			Mixture (A)	Nicotine alone		Adjunct alone 5 percent (D)	(A - (C + D))	(A - B)
				5 percent[1/] (B)	2 percent (C)			
Aroclor 1232:								
Armyworm	100	Moderate	100	97	31	-	-	+ 3
	110	-do-	97	97	83	70	-56	0
Diamondback moth	104	None	100	97	67	-	-	+ 3
	68	-do-	90	77	10	20	+60	+13
Pea aphid	118	-	23	56	12	-	-	-33
		Av.	82	85			+ 2	+ 3
bis-(p-bromophenyl) sulfide:								
Armyworm	105	Moderate	7	52	0	-	-	-45
	129	Trace	64	77	13	-	-	-13
	94	-do-	100	100	58	-	-	0
Diamondback moth	95	Moderate	24	60	14	-	-	-36
	110	-do-	36	75	26	-	-	-39
Pea aphid	108	-	99	95	54	-	-	+ 4
	105	-	100	75	52	-	-	+25
		Av.	61	76				-15
bis(p-chlorophenyl) disulfide:								
Armyworm	100	Moderate	86	92	25	-	-	- 6
	105	-do-	72	97	58	-	-	-25
Diamondback moth	100	-do-	52	97	16	-	-	-45
	91	-do-	56	78	34	-	-	-22

Green dock beetle	100	-do-	92	94	81	-	-	- 2
	78	-do-	71	78	19	-	-	- 7
Pea aphid	117	-	22	71	48	-	-	-49
	110	-	5	66	47	-	-	-61
	125	-	38	66	47	0	- 9	-28
		Av.	55	82				-27
Dibenzothiophene, 2-chloro-:								
Armyworm	100	Moderate	92	97	31	-	-	- 5
	104	-do-	100	97	83	90	-73	+ 3
Diamondback moth	103	Trace	97	97	67	-	-	0
	63	None	97	77	10	11	+76	+20
Pea aphid	122	-	20	56	12	-	-	-36
		Av.	81	85			+ 2	- 4
Dibenzothiophene, monochloro:								
Armyworm	103	Moderate	100	97	31	-	-	+ 3
	104	None	100	97	83	90	-73	+ 3
Diamondback moth	102	-do-	100	97	67	-	-	+ 3
	62	-do-	100	77	10	97	- 7	+23
Pea aphid	125	-	25	56	12	-	-	-31
		Av.	85	85			-40	0
Fluorene:								
Armyworm	90	Trace	84	71	0	-	-	+13
	90	None	100	100	58	-	-	0
Diamondback moth	95	Moderate	13	31	16	-	-	-18
Pea aphid	105	-	35	30	9	-	-	+ 5
		Av.	58	58				0

1/ 3.5 percent of nicotine used as the standard against the pea aphid.

Table 1.--(Continued)

Adjunct and insect	Deposit of dust mixture (micrograms per square centimeter)	Extent of feeding	Percent mortality					
			Mixture (A)	Nicotine alone		Adjunct alone 5 percent (D)	(A - (C + D))	(A - B)
				5 percent[1] (B)	2 percent (C)			
Isophthalonitrile:								
Armyworm	90	None	100	100	58	-	-	0
	100	-do-	100	100	58	-	-	0
	90	-do-	97	94	44	-	-	+ 3
Diamondback moth	121	Moderate	46	60	15	-	-	-14
Pea aphid	115	-	95	66	47	-	-	+29
	120	-	53	71	48	-	-	-18
		Av.	82	82				0
Methyleneaminoacetonitrile:								
Armyworm	135	Trace	97	73	45	-	-	+24
	120	Moderate	78	100	64	6	+ 8	-22
	100	None	100	100	58	-	-	0
	104	Trace	97	97	42	11	+44	0
	123	Moderate	89	100	67	0	+22	-11
Diamondback moth	102	Trace	94	97	67	-	-	- 3
	95	-do-	94	100	86	-	-	- 6
Pea aphid	108	-	75	66	47	-	-	+ 9
	102	-	83	48	33	2	+48	+35
		Av.	90	87			+30	+ 3
alpha-Naphthonitrile:								
Armyworm	95	None	100	94	58	-	-	+ 6
	163	-do-	100[2]	8	8	-	-	+92
	117	Moderate	94[2]	0	0	64	+30	+94

Diamondback moth	112	None	100	100	94	-	-	0
	90	Trace	86	94	53	-	-	- 8
Pea aphid	120	-	76	66	47	-	-	+10
		Av.	93	60			+30	+32
m-Nitrobenzonitrile:								
Armyworm	94	Moderate	83	97	31	-	-	-14
	92	None	100	100	58	-	-	0
	107	-do-	97	100	64	97	-64	- 3
	128	Moderate	67[2/]	0	0	43	+24	+67
	100	None	100	97	42	53	+ 5	+ 3
	116	Trace	97	100	67	75	-45	- 3
Diamondback moth	120	Moderate	47	60	15	-	-	-13
Pea aphid	112	-	86	66	47	-	-	+20
	108	-	44	71	48	-	-	-27
	112	-	79	48	33	20	+26	+31
		Av.	80	74			-20	+ 6
Phenyl sulfoxide:								
Armyworm	102	Moderate	100	78	67	-	-	+22
	106	None	97	100	64	36	- 3	- 3
	100	-do-	100	97	42	89	-31	+ 3
	125	-do-	100	100	67	83	-50	0
Diamondback moth	108	-do-	100	83	39	-	-	+17
	90	Trace	92	97	53	-	-	- 5
	106	None	100	100	86	-	-	0
Pea aphid	120	-	46	66	47	-	-	-20
	117	-	23	48	33	0	-10	-25
		Av.	84	85			-24	- 1
Tall oil nitrile:								
Armyworm	90	Trace	97	100	58	-	-	- 3
	102	Moderate	47	97	50	-	-	-50
	109	-do-	58	100	64	0	- 6	-42
	110	-do-	33	97	42	17	-26	-64
	130	-do-	67	100	67	0	0	-33
Diamondback moth	108	-do-	83	100	85	-	-	-17
Pea aphid	120	-	69	71	48	-	-	- 2
	120	-	6	48	33	0	-27	-42
		Av.	58	89			-20	-32

2/ Fumigation test.

Table 2. --Adjuncts in mixture with nicotine showing synergism against one insect only

Adjunct	Armyworm	Diamondback moth	Pea aphid
Acrylonitrile	-	x	-
n-Butyronitrile	-	x	-
delta-Chlorovaleronitrile	-	-	x
Coco nitrile (Arneel CD)	x	-	-
Cyanamid	-	-	x
Cyanoacetanilide	-	x	-
alpha-Cyanoethyl acetate	-	-	x
Cyanuric acid	-	-	x
Decane nitrile (Arneel 10D)	x	-	-
Dicapryl tetrahydrophthalate	-	-	x
Diethyl phthalate	-	-	x
Ethoxypropionitrile	-	-	x
Lactonitrile	-	-	x
Lauryl cyanide	-	-	x
alpha-Naphthaleneacetonitrile	-	-	x
p-Nitrobenzonitrile	-	-	x
p-Nitrophenylacetonitrile	x	-	-
Phthalamide	-	-	x
Pivalonitrile	-	-	x
Tetradecane nitrile (Arneel 14D)	-	x	-
Thianthrene	-	x	-
Tribromophenyl sulfide	-	-	x
Triethyl phosphate	x	-	-